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# Investigating Chemical and Molecular Changes in Uranium Oxyfluoride Particles using NanoSIMS and Micro-Raman Spectroscopy

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**Abstract.** Processes involving the treatment of nuclear material inherently release small amounts of this material to the environment. Environmental sampling is therefore an important tool in the detection of undeclared nuclear activities. Environmental samples taken at enrichment facilities typically contain particles of uranium oxyfluoride ( $\text{UO}_2\text{F}_2$ ) formed from the hydrolysis of  $\text{UF}_6$ . Somewhat surprisingly, these samples were also found to contain uranium-bearing particles without a measurable amount of fluorine, suggesting  $\text{UO}_2\text{F}_2$  is unstable with respect to the loss of fluorine. As environmental sampling depends upon laboratory analysis of nuclear material that has often been exposed to the environment after it was produced, it is important to understand how those environmental conditions might have changed the material over time. Previous studies have shown that exposure to high temperature, high relative humidity and ultraviolet light accelerates the loss of fluorine in  $\text{UO}_2\text{F}_2$  particles, yet the conditions under which this occurs and the chemical and molecular changes that result from this decomposition are not well understood. This work aims to provide a better understanding of the chemical and molecular changes in  $\text{UO}_2\text{F}_2$  particles from the exposure to specific environmental conditions, and in particular from the exposure to air of different relative humidity. To this end,  $\text{UO}_2\text{F}_2$  particulate material was prepared from the controlled hydrolysis of  $\text{UF}_6$  expressly for the purpose of these experiments. Particles were measured by ultrahigh spatial resolution secondary ion mass spectrometry (NanoSIMS) and micro-Raman spectroscopy before and after exposure to air at different relative humidity. These measurements demonstrated that even though the decomposition of  $\text{UO}_2\text{F}_2$  is very slow, NanoSIMS and Raman spectroscopy can be applied to distinguish subtle differences depending on the environment to which the samples were exposed. The experiments described in this paper also demonstrated that a combination of analytical techniques is the best approach to characterize  $\text{UO}_2\text{F}_2$  particles produced from  $\text{UF}_6$  hydrolysis.

## 1. Introduction

Uranium oxyfluoride ( $\text{UO}_2\text{F}_2$ ) is a compound formed from the hydrolysis of uranium hexafluoride ( $\text{UF}_6$ ) [1,2]. Gaseous  $\text{UF}_6$  is processed at uranium enrichment facilities where  $\text{UF}_6$  is enriched in the U-235 isotope for the purpose of producing nuclear reactor fuel. Given the very reactive nature and the large amounts of  $\text{UF}_6$  used at these facilities, very small releases to the atmosphere are common, and result in the formation of  $\text{UO}_2\text{F}_2$  particulate material and HF [1,2].

Environmental sampling for nuclear safeguards is based on the analysis of this type of particulate fall out material. The method is very effective: the particles are representative of the source material, and since they are difficult to remove, they can provide insights into the history of a facility's operations [3]. The environmental swipe samples are sent to the analytical labs of the IAEA and Euratom, where the uranium particulate material is measured for its isotopic composition [3]. The range of uranium isotopic compositions that result from these measurements are compared to the facilities' declarations, in order to verify the absence of undeclared activities.

Even though mass spectrometric analysis of the uranium isotopic composition is the main method used in environmental sampling, additional information on the particles' source, formation process and exposure history can be obtained from elemental, molecular and morphological analysis. The elemental analysis of environmental samples from enrichment facilities has shown to contain uranium-bearing particles with and without a measurable amount of fluorine [4]. This seemed to suggest that  $\text{UO}_2\text{F}_2$  loses its fluorine

from the exposure to certain environmental conditions. A previous study by Carter et al. [2] has also demonstrated that the exposure to high temperature, high relative humidity and ultraviolet light accelerates the loss of fluorine in  $\text{UO}_2\text{F}_2$ . However, the exact conditions under which this happens and the chemical and molecular changes that accompany this decomposition are not well understood.

This work aims to provide a better understanding of the chemical and molecular changes in  $\text{UO}_2\text{F}_2$  particles from the exposure to specific environmental conditions, and in particular from the exposure to air of different relative humidity. All samples for this study were prepared from the hydrolysis of gaseous  $\text{UF}_6$  in a humid atmosphere. The small particle size required the use of highly sensitive and selective analytical tools. We therefore applied both nanoscale secondary ion mass spectrometry (NanoSIMS) and micro-Raman spectroscopy to a set of particulate samples. The NanoSIMS mass spectrometer has a special resolution of up to 50 nm for negative ion analysis ( $\text{Cs}^+$  bombardment) or 150-200 nm for positive ion analysis ( $\text{O}^-$  bombardment). The Raman set up has a spatial resolution in the micrometer range, which is substantially better than micro-infrared (20-400  $\mu\text{m}$ ) or micro-XRF (50-3000  $\mu\text{m}$ ) [5]. From the combined elemental and spectral information obtained from these measurements we were able to draw conclusions on the effect of relative humidity on  $\text{UO}_2\text{F}_2$ .

## 2. Experimental

### 2.1 Uranyl difluoride ( $\text{UO}_2\text{F}_2$ ) particulate material

The  $\text{UO}_2\text{F}_2$  particulate material used for this work was prepared at the Institute for Reference Materials and Measurements (IRMM, European Commission, Joint Research Centre, Geel, Belgium) expressly for the purpose of these experiments. An apparatus, called the aerosol deposition chamber, was used to produce  $\text{UO}_2\text{F}_2$  particles from the hydrolysis of gaseous  $\text{UF}_6$  [6]. It should be noted however, that we have no evidence that fugitive emissions from a uranium enrichment facility would, or would not, appear similar to the analyzed samples.

Since the uranium isotopic composition of the  $\text{UO}_2\text{F}_2$  material was not of interest to this study, depleted  $\text{UF}_6$  with a  $^{235}\text{U}$  abundance of 0.28 % was used to simplify sample manipulations. About 40 mg of  $\text{UF}_6$  was released inside the aerosol deposition chamber in high humidity air. Upon release in the chamber, the  $\text{UF}_6$  quickly hydrolyzes to HF and particulate  $\text{UO}_2\text{F}_2 \cdot n\text{H}_2\text{O}$ , with  $n$  varying between 1.5 and 4 (Eq. 1) [7,8]. Details on the reaction kinetics can be found in [9].

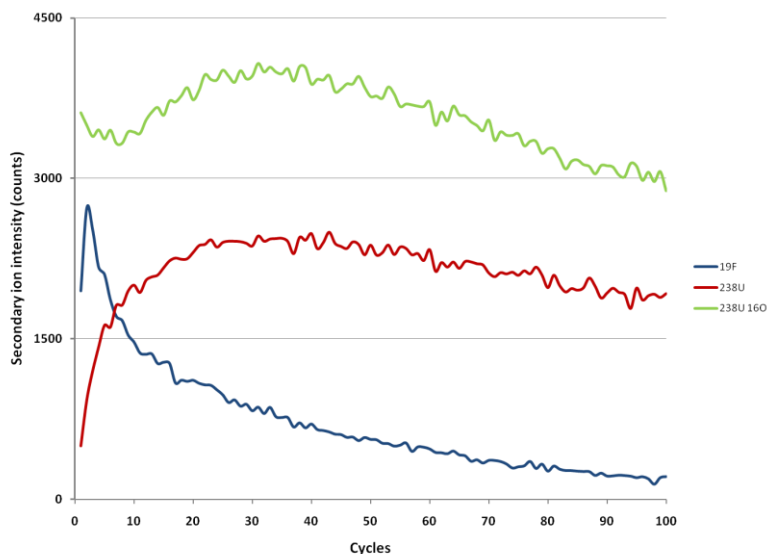


The uranyl difluoride particles were collected on 9.5 mm diameter graphite planchets (Ernest F. Fullam, New York, USA) through gravitational settling. These graphite planchets were taken out of the aerosol deposition chamber after the particulate fall out material had settled, and were then stored in containers filled with argon for shipment to Lawrence Livermore National Laboratory (LLNL, US Department of Energy, Livermore, California, USA). The  $\text{UO}_2\text{F}_2$  particle samples were exposed to specific temperature, humidity and lighting conditions in a set of environmental chambers (ETS and ThermoForma, USA). This paper focuses on the effects of relative humidity on  $\text{UO}_2\text{F}_2$ . The relative humidity (RH) in the chambers was set from less than 15 % up to 70 %. The exact conditions and duration of the exposure are specified for each experiment individually. The results from the exposure to high temperature and ultraviolet light are published elsewhere [10,11].

## 2.2 Nanometer scale Secondary Ion Mass Spectrometry (NanoSIMS)

The NanoSIMS 50 (Cameca, France) is a secondary ion mass spectrometer that produces ion images of exceptionally high spatial resolution. The combination of a short working distance, normal ion beam incidence and high brightness ion source results in a lateral resolution in the order of a few hundred nanometers (compared to several microns for conventional SIMS instruments). The  $\text{UO}_2\text{F}_2$  particles were measured by a 16 keV beam of  $\text{O}^-$  ions produced by a duoplasmatron directed onto the sample in a raster pattern. The primary ion beam current at the sample varied between 25 pA - 130 pA, depending on the lens that was used to collimate the primary  $\text{O}^-$  ions. The primary ion beam was measured to have a spot size of about 300-400 nm. The positively-charged secondary ions that were produced by the sputtering process were separated and detected by a double-focusing mass analyzer. A  $\text{UF}_4$  sample was used for mass calibration. The mass resolution for uranium was around 6500. Ion conversion and transmission were calculated from the measurement of the  $\text{Al}^+$  secondary ion intensity of an Cu-Al sample, and were both in the acceptable range (1.9 % and 60 % respectively).

The intensity of the  $\text{F}^+$  and  $\text{U}^+$  secondary ions was measured to calculate the relative amount of fluorine in samples exposed to different levels of relative humidity (Fig. 1). Since the graphite substrates were found to contain fluorine particles with no uranium, large area ( $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ ) real-time imaging of the  $\text{UO}^+$  ions, which are initially more intense than the  $\text{U}^+$  ions, was used to locate and center the uranium particles of interest. For the analysis, the raster size was reduced to  $6\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$ , with an image resolution of  $64 \times 64$  or  $128 \times 128$  pixels. Ion images were obtained from the correlation of the beam position with the secondary ion intensity (Fig. 2).



**Fig 1:** NanoSIMS depth profile showing the  $\text{F}^+$ ,  $\text{U}^+$  and  $\text{UO}^+$  secondary ions as a function of sputtering time. The  $\text{U}^+$  and  $\text{UO}^+$  ions have a similar profile and reach their maximum intensity at the same point in the analysis, while the  $\text{F}^+$  ions reach their maximum shortly after sputtering has started, and follow a steep decrease after that.

A depth profile was produced by measuring the  $\text{F}^+$ ,  $\text{U}^+$  and  $\text{UO}^+$  ion intensity during sputtering. The  $\text{F}^+$ ,  $\text{U}^+$  and  $\text{UO}^+$  ions were recorded while cycling the magnetic field of the analyzer (peak jumping). The analysis was stopped at the point where the  $\text{F}^+$  secondary ion count rate dropped to background values (Fig. 1). The fluorine-to-uranium ( $\text{F}^+/\text{U}^+$ ) ratio was then calculated from the summed ion counts for  $\text{F}^+$  and  $\text{U}^+$  integrated over the total duration of the analysis. Between 3 and 7 areas were analyzed per sample. The average value of the  $\text{F}^+/\text{U}^+$  ratio and its 1 sigma standard error were used to evaluate the variability within each sample and between samples exposed to different relative humidity. Specific image processing software (L'Image, Larry Nittler) was used for data reduction.

## 2.3 Micro-Raman spectroscopy

The micro-Raman measurements were performed using 632.8 nm (red) excitation produced by a HeNe laser. The laser light was directed towards the sample using a laser band pass cube focused with a 100× apochromatic objective lens (Mitutoyo, Japan) to a spot on the sample with an estimated diameter of 1  $\mu\text{m}$ . The laser power was varied using neutral density filters to maximize sensitivity without damaging the particles. Scattered light was collected with the same objective and was focused onto a pinhole before being directed into the spectrometer (Horiba Jobin Yvon HR460, Japan). Holographic filters were used to reject elastically scattered laser light.

High resolution spectra were acquired using an 1800 lines/mm grating. The position of the spectral lines produced by a neon lamp were recorded for calibration purposes. This said however, the width of the Raman peaks produced by the samples was generally much larger than the spectral resolution, therefore small instrumental non-linearities were ignored. Also, no correction was made over the relatively small spectral range for variations in instrumental sensitivity. Peak fitting of the asymmetrical uranyl peaks has not been attempted here. The indicated frequencies of the Raman bands represent the estimated positions of the maximum Raman scatter intensity. Five to 7 particles were analyzed per sample. Up to 7 spectra were obtained from each particle. The acquisition time for the high resolution spectra varied between 1 and 10 minutes, and is specified for each of the spectra shown below.

## 3. Results and Discussion

### 3.1 NanoSIMS

#### 3.1.1 Samples stored in an inert atmosphere

The NanoSIMS 50 was applied here to provide elemental and quantitative information on the decomposition of  $\text{UO}_2\text{F}_2$  due to humidity exposure. The intensity of the  $\text{F}^+$  and  $\text{U}^+$  secondary ions was measured to calculate the relative amount of fluorine in samples exposed to different levels of relative humidity. The effect of relative humidity on the  $\text{F}^+/\text{U}^+$  ratio in  $\text{UO}_2\text{F}_2$  particles could only be assessed however, when compared to a reference value. A set of 6 samples that had not been exposed to humidity (after preparation) was therefore kept in argon or nitrogen and analyzed by NanoSIMS after 3-4 months of storage. The  $\text{F}^+/\text{U}^+$  ratio for this sample set ranged from  $0.21 \pm 0.02$  to  $0.77 \pm 0.14$ . As presented in Table 1, these samples showed a fairly large variation in the  $\text{F}^+/\text{U}^+$  ratio, even for samples prepared during the same release of  $\text{UF}_6$ . This variation may either result from differences in particle morphology, topography or charging of the sample, or could be characteristic of the particle formation process (gas-phase condensation).

#### 3.1.2 Samples stored in dry air

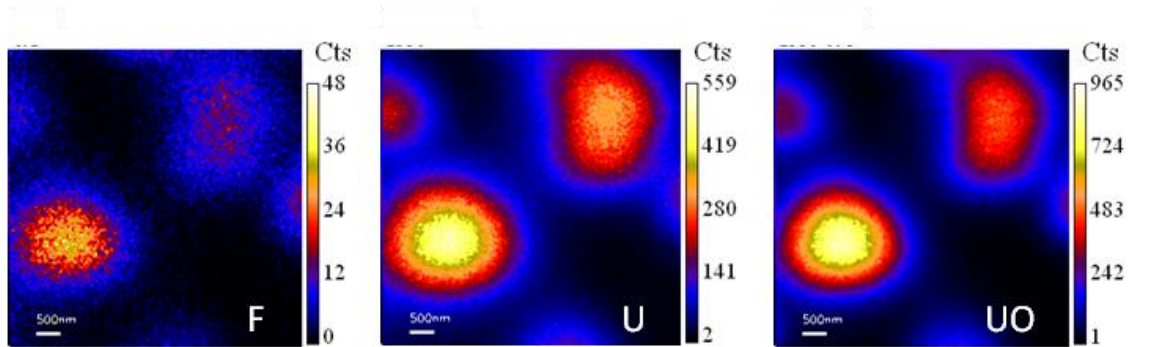
$\text{UO}_2\text{F}_2$  is known to be highly hygroscopic, and is already partially hydrated at the time of formation in the aerosol deposition chamber (Eq. 1). Storage in dry air was therefore assumed to preserve the initial particle composition. A subset of the samples was not kept in an inert atmosphere after preparation, but instead stored in air of less than 15 % RH. The overall  $\text{F}^+/\text{U}^+$  ratio of these samples varied between  $0.09 \pm 0.01$  and  $0.14 \pm 0.05$  when measured between 3 weeks and 3 months of storage. The variability was again large, but the  $\text{F}^+/\text{U}^+$  ratio was generally lower than for the samples stored in argon or nitrogen. This seemed to suggest that the partially hydrated  $\text{UO}_2\text{F}_2$  is affected by interactions with the atmosphere, even at very low levels of relative humidity. Over a timescale of one year however, the  $\text{F}^+/\text{U}^+$  ratio did not decrease significantly compared to the initial range of values, indicating that the decomposition of  $\text{UO}_2\text{F}_2$  has either stabilized or occurs at a very slow rate when exposed to dry air.

### 3.1.3 Samples stored in air with 30-45 % RH

Only a few samples were exposed to air at intermediate relative humidity and the results obtained from NanoSIMS analysis were not very conclusive. The measurement of 7 particles on a sample that was stored in 30 % RH for 10 weeks resulted in an average  $F^+/U^+$  ratio of  $0.036 \pm 0.009$ , which is lower than what was measured for the samples stored in dry air. Then again, the measurement of a sample that was stored in 43 % RH for 8 weeks produced an average value of  $0.068 \pm 0.013$ , about a factor 2 higher than what was obtained from the 30 % exposure sample. From these measurements it was concluded that, given the large variability between samples, a larger data set needs to be evaluated, and measurement before and after humidity exposure is required to be able to draw meaningful conclusions on the rate of fluorine loss under these humidity conditions.

### 3.1.4 Samples stored in air with 70-76 % RH

Given the slow nature of the decomposition of  $UO_2F_2$  at lower levels of relative humidity, an initial set of 5 particle samples was exposed to 76 % RH for a duration between 4 and 7 months. Under these exposure conditions, the intensity of the  $F^+$  secondary ions was not more than 10-50 counts per second, with the count rate dropping even further after just a few minutes of sputtering. The total counts for  $F^+$  were therefore very low, and resulted in very large variability of  $F^+/U^+$  ratios ( $0.0007 \pm 0.0005$  -  $0.009 \pm 0.002$ ). Two additional samples were hence stored in 70 % RH air for much shorter exposure times: NanoSIMS analyses before and after exposure to 70 % RH for 18 hours showed a drop in the average  $F^+/U^+$  ratio from  $0.65 \pm 0.07$  to  $0.26 \pm 0.02$ , which is a decrease of 60 %. As expected, the decrease was even more pronounced for an exposure of 117 hours (Fig. 2), where the ratio dropped by 94 % from  $0.77 \pm 0.14$  to  $0.52 \pm 0.003$ . It should be noted that in both cases the final  $F^+/U^+$  ratio was still higher than what was measured for the samples stored in dry air. The samples for the high humidity experiment however, had a very high initial  $F^+/U^+$  ratio, and were exposed to high humidity for only short amounts of time (a maximum of 5 days instead of 3 months). This experiment did emphasize the importance of measuring the same sample before and after humidity exposure, due to the high initial variation on the  $F^+/U^+$  ratio.



**Fig 2:** 6 µm x 6 µm ion images ( $F^+$ ,  $U^+$ ,  $UO^+$ ) of  $UO_2F_2$  particles exposed to 117 hours of 70 % relative humidity.

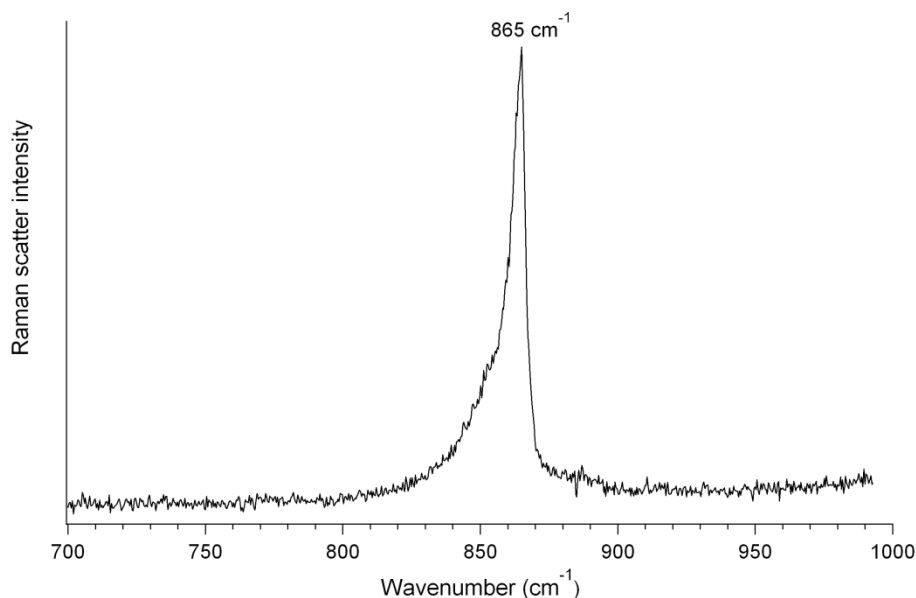
Storage conditions	Duration	Minimum $F^+/U^+$ ratio	Maximum $F^+/U^+$ ratio
Argon (inert)	3 - 4 months	$0.21 \pm 0.02$	$0.77 \pm 0.14$
Dry air of less than 15 % RH	3 weeks - 7 months	$0.09 \pm 0.01$	$0.14 \pm 0.05$
30 % - 43 % RH	2 - 2.5 months	$0.036 \pm 0.009$	$0.068 \pm 0.013$
70 % - 76 % RH	4 - 7 months	$0.0007 \pm 0.0005$	$0.009 \pm 0.002$

**Table 1:** Range of  $F^+/U^+$  ratios obtained from NanoSIMS analyses for the different storage conditions (long term)

## 3.2 Micro-Raman spectroscopy

### 3.2.1 Samples stored in an inert atmosphere

Also for these measurements, the Raman spectrum from a ‘pristine’ sample stored in argon since its preparation at the IRMM was used as a baseline for comparison with samples exposed to different levels of relative humidity. The Raman bands of this baseline sample were very strong, even at a power setting of 0.52 mW (measured at the sample), and were in agreement with what is published on hydrated  $\text{UO}_2\text{F}_2$  [12]. The uranyl ( $\text{UO}_2$ )<sup>2+</sup> symmetric stretching frequency around  $865\text{ cm}^{-1}$  was the most prominent peak in the spectrum, with a shoulder towards the lower frequency side (Fig. 3). At lower Raman shifts (not shown), a peak around  $180\text{ cm}^{-1}$  was detected, attributed to the U-O bend.

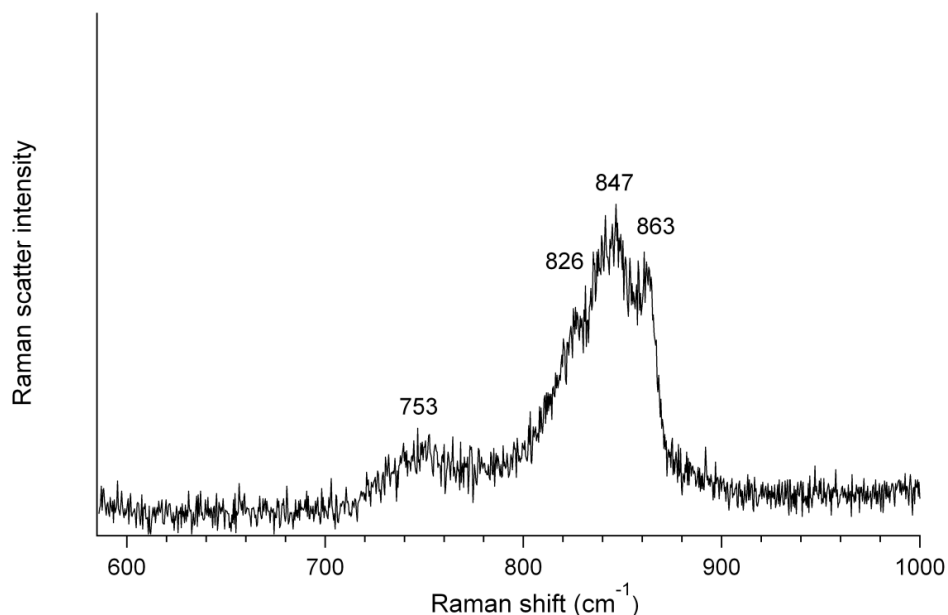


**Fig. 3:** High resolution Raman spectrum (300s acq. time, 0.52 mW) of a  $\text{UO}_2\text{F}_2$  particle kept in an argon atmosphere for 7 months showing a distinct, asymmetrical peak around  $860\text{ cm}^{-1}$  attributed to the ( $\text{UO}_2$ )<sup>2+</sup> symmetric stretch.

### 3.2.2 Samples stored in dry air

The spectrum of a  $\text{UO}_2\text{F}_2$  particle sample kept in an argon atmosphere for several months followed by storage in dry air with a relative humidity of not more than 25 % was expected to look similar to the spectrum described above. The typical uranyl peak was still detected, this time around  $863\text{ cm}^{-1}$ , yet an additional peak with a shoulder on the lower frequency side appeared in the spectrum at around  $845\text{ cm}^{-1}$  (Fig. 4). This peak was generally stronger and broader than the peak at  $863\text{ cm}^{-1}$ , still the small difference in Raman shift seemed to suggest that both peaks resulted from the uranyl symmetric stretch.  $\text{UO}_2\text{F}_2$  has a layered structure, with the planes of uranium separated by  $5.22\text{ \AA}$  and the axis of the uranyl group normal to these planes. This structure allows the insertion of water molecules between the layers and therefore a series of uranyl difluoride hydrates are known [13]. A change in hydration state may have led to the shift of the peak at  $863\text{ cm}^{-1}$  towards lower frequencies. This distortion of the lattice structure typically results in peak broadening, which may explain the broadness of the peak at  $847\text{ cm}^{-1}$ . In addition, a broad and weak feature was detected around  $753\text{ cm}^{-1}$ .

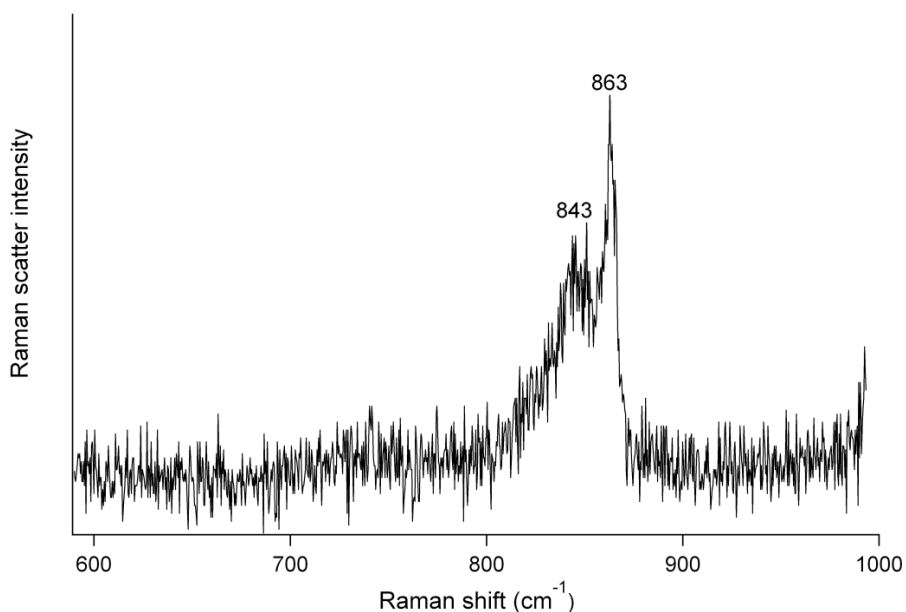




**Fig. 4:** Raman spectrum (1800 l/mm, 5 x 60s acq. time, 0.23 mW) of a  $\text{UO}_2\text{F}_2$  particle stored in Ar and dry air.

### 3.2.3 Samples stored in air with 30-45 % RH

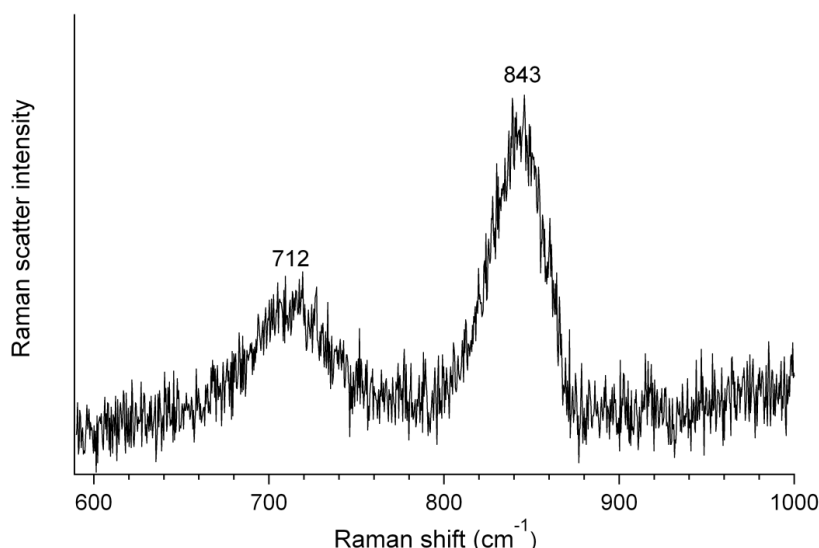
The spectrum of a sample exposed for 3 months to air at room temperature and 30 % relative humidity showed the uranyl peak at the same position as in the baseline spectrum, i.e. around  $863\text{ cm}^{-1}$ . In addition however, a less intense but distinct band appeared around  $843\text{ cm}^{-1}$  (Fig. 5). The close proximity of both peaks may imply that the band at  $843\text{ cm}^{-1}$  was also produced by the  $(\text{UO}_2)^{2+}$  stretching frequency, but in a different hydration state.



**Fig. 5:** High resolution Raman spectrum (60s acq. time, 0.8 mW) of a  $\text{UO}_2\text{F}_2$  particle stored in 30 % RH for 3 months.

### 3.2.4 Samples stored in air with 70-76 % RH

After an exposure to 70 % relative humidity for 117 hours, the initial uranyl peak around  $863\text{ cm}^{-1}$  could no longer be resolved and the band around  $843\text{ cm}^{-1}$  had become the most distinct feature in the spectrum (Fig. 6). These measurements suggest that the uranyl peak which was detected around  $863\text{ cm}^{-1}$  in the baseline spectrum, broadened and shifted towards lower frequencies due to the absorption of water. This finding confirms our conclusions from NanoSIMS analyses where high relative humidity exposure drastically altered the chemical composition of  $\text{UO}_2\text{F}_2$ , even after short exposure times.



**Fig. 6:** High resolution Raman spectrum (2 x 300s acq. time, 0.16 mW) of a  $\text{UO}_2\text{F}_2$  particle stored in 70 % RH for 117 hours. The peak at  $843\text{ cm}^{-1}$  was the dominant peak in the spectrum, with an additional broad band around  $712\text{ cm}^{-1}$ .

## 4. Conclusions

The experiments described in this paper demonstrated that a combination of complementary analytical techniques is the best approach to characterize  $\text{UO}_2\text{F}_2$  particles produced from  $\text{UF}_6$  hydrolysis. The small particle size (typically less than a micrometer) required the use of highly sensitive and selective analytical tools. NanoSIMS and micro-Raman spectroscopy were used to characterize the baseline  $\text{F}^+/\text{U}^+$  ratio and Raman bands of hydrated  $\text{UO}_2\text{F}_2$ . These measurements were then compared to the results obtained from samples exposed to varying degrees of relative humidity. Even though the baseline samples showed a large variability in the  $\text{F}^+/\text{U}^+$  ratio, a significant decrease in the relative amount of fluorine was detected for samples exposed to high humidity. In the spectra obtained by micro-Raman spectroscopy, the decomposition of  $\text{UO}_2\text{F}_2$  due to humidity exposure was manifested in peak broadening and shifts towards lower frequencies. This molecular fingerprinting was found to be a valuable complement to the NanoSIMS data, where the effect of humidity exposure was not always unambiguous due to the large variability on the  $\text{F}^+/\text{U}^+$  ratios.

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